

# **Growth and Characterization of single crystal InAs nanowire arrays and their application to plasmonics**

S.M. Prokes, H.D. Park\* and O.J. Glembocki

US Naval Research Laboratory

4555 Overlook Ave. SW, Washington DC 20375

\*ASEE post doctoral fellow, Naval Research Lab

**Keywords:** InAs nanowires, VLS growth, Raman spectroscopy, SERS

## **ABSTRACT**

The growth of single crystal InAs nanowire arrays on crystalline and amorphous substrates is described. This method is quite simple and fast, and uses only a bare InAs substrate as a source and a gold colloid on the growth substrate. High quality InAs nanowires can be produced by this technique, with the nanowire diameter controllable by the gold colloid size and the nanowire length controlled by the growth time and growth temperature. By a proper choice of substrate, parallel, non-interacting nanowire arrays can be formed, as well as arrays exhibiting a cross-over geometry. These geometries can have a significant impact on the plasmonic properties, specifically on surface enhanced Raman (SERS). Results indicate a significantly enhanced SERS signal for nanowire arrays which contain wire crossings, which is explained in terms of electric field “hot” spots.

## **1. INTRODUCTION**

InAs is an attractive semiconductor for application in high performance electronics due to its high electronic mobility, as well as surface accumulation. Several methods of InAs nanowire

Report Documentation Page			Form Approved OMB No. 0704-0188		
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE <b>2006</b>	2. REPORT TYPE		3. DATES COVERED <b>00-00-2006 to 00-00-2006</b>		
4. TITLE AND SUBTITLE <b>Growth and Characterization of single crystal InAs nanowire arrays and their application to plasmonics</b>			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, DC, 20375</b>			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>Proceedings of the SPIE, v. 6370, 63700Q-1, (2006)</b>					
14. ABSTRACT <b>The growth of single crystal InAs nanowire arrays on crystalline and amorphous substrates is described. This method is quite simple and fast, and uses only a bare InAs substrate as a source and a gold colloid on the growth substrate. High quality InAs nanowires can be produced by this technique, with the nanowire diameter controllable by the gold colloid size and the nanowire length controlled by the growth time and growth temperature. By a proper choice of substrate, parallel, non-interacting nanowire arrays can be formed, as well as arrays exhibiting a cross-over geometry. These geometries can have a significant impact on the plasmonic properties, specifically on surface enhanced Raman (SERS). Results indicate a significantly enhanced SERS signal for nanowire arrays which contain wire crossings, which is explained in terms of electric field "hot" spots.</b>					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>Same as Report (SAR)</b>	18. NUMBER OF PAGES <b>10</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

growth have been reported, including metalorganic vapor phase epitaxy (MOVPE)<sup>1</sup> and chemical beam epitaxy (CBE)<sup>2</sup>, in which the wires were grown epitaxially with the substrate. The growth of loose InAs wires has also been reported by laser-assisted catalytic growth (LCG)<sup>3</sup> and a vapor method using In metal and a GaAs substrate, with a growth time of 36 hours.<sup>4</sup> In our work, we have reported a very simple and inexpensive method to grow InAs nanowires epitaxially on an InAs(111) wafer<sup>5</sup>. This growth technique results in high quality, stoichiometric InAs wires, and there is no need to prefabricate complex target materials, use toxic gases or solid As sources, nor subject the sample to lengthy growth times.

We have extended this growth technique to produce arrays of epitaxial InAs nanowires, as well as 3D random arrays of nanowires on various other substrates, including InAs, miscut 5° from (111), Si(111) and SiO<sub>2</sub>. We can control the size and uniformity of the resultant nanowires by the use of a gold colloid, and the colloid distribution determines the InAs nanowire array. Since we can control the geometry and size of the nanowires in the growth process, we can use these templates to examine other effects, such as plasmonics. We will discuss the effect of nanowire array geometry on the plasmonic effects of surface enhanced Raman (SERS), and the results will show the importance of cross-over geometry to maximize the SERS effect.

## **2. EXPERIMENTAL PROCEDURE**

The InAs nanowires were grown inside a sealed quartz tube in an open tube furnace, as described previously<sup>5</sup>. The InAs substrates were first etched in HCl to remove any native oxide, and then gold colloid (Ted Pella, Inc.) drops were placed on the growth substrate, using poly L-lysine, which allows the deposition of a uniform distribution of gold nanoparticles on the surface. In the case of silicon and SiO<sub>2</sub> substrates, dilute HF solution was used to strip the oxide layer, prior to the L-lysine treatment. The substrate was immediately loaded, along with a bare InAs source substrate, inside a quartz tube, which was evacuated to 70 mTorr and sealed with a torch. The center of the furnace was raised to the growth temperature, which ranged from 400°C to 660°C, and the quartz tube was inserted into the hot furnace. Inside the quartz tube, the source InAs substrate was positioned at the hottest point in the furnace, while the gold-colloid coated substrate was placed toward the cooler end of the furnace, where the temperature could be adjusted to specific growth

conditions. After a set growth time, the quartz tube was immediately removed from the hot furnace and cooled in water. The grown nanowires were analyzed using a LEO SUPRA 55 scanning electron microscope (SEM), JEOL 2010F 200 KV high resolution transmission electron microscope (HRTEM) and X-ray energy dispersive spectroscopy (EDS) attached to the HRTEM.

### 3.1 GROWTH OF InAs NANOWIRE ARRAYS ON InAs (111) SUBSTRATE

An image of the nanowires grown inside the sealed quartz tube using 5nm, 20nm, 60nm or 100nm gold colloids, respectively, is shown in Fig. 1a-d. In this case, the substrate was InAs(111)

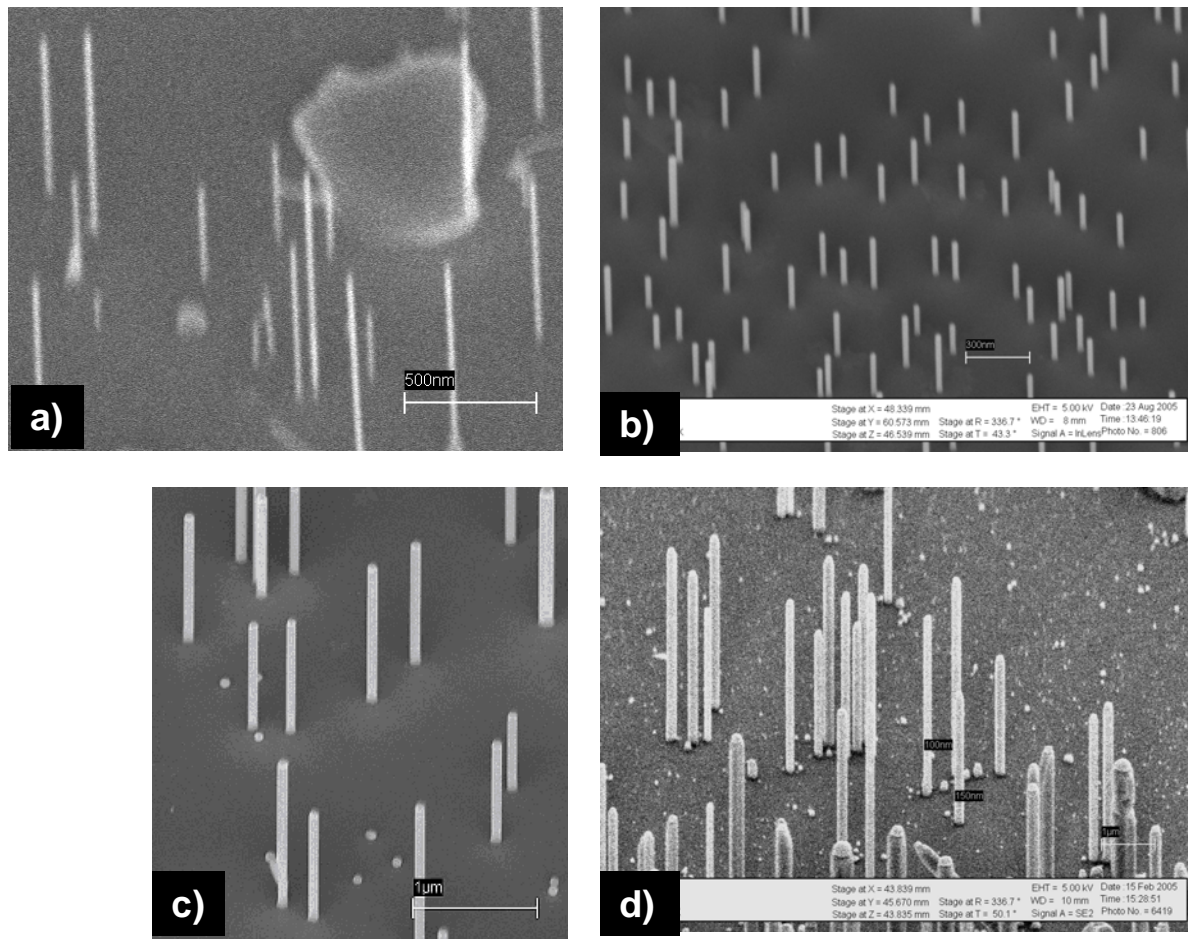
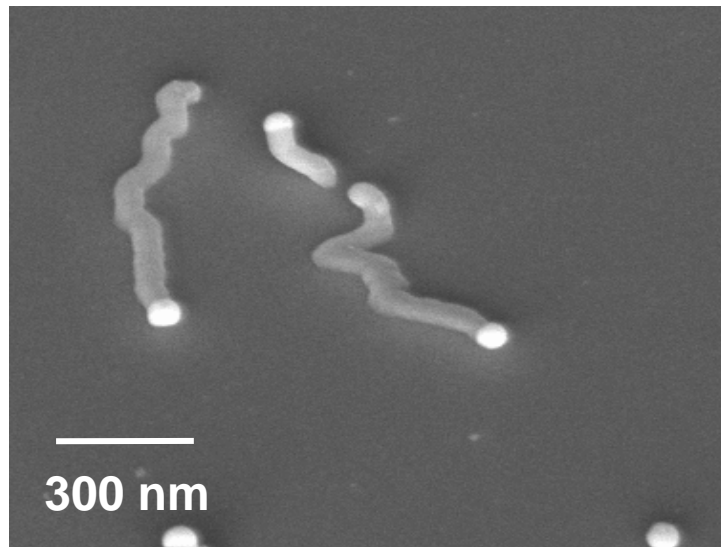


Figure 1: Growth of epitaxial InAs nanowire arrays on InAs(111) substrate for a) 5nm Au colloid, b) 20nm colloid, c) 60nm colloid and d) 100nm colloid.

and the nanowires grew epitaxially, perpendicular to the (111) substrate plane. Note that the nanowires are of uniform diameter, corresponding to the specific gold colloid size used. Each nanowire terminates with an Au-In colloid tip, as would be expected from the VLS mechanism. Nanowire growth was noted for a large temperature range, as low as 400°C (which is below the bulk eutectic of 450°C<sup>6</sup>) to as high as 660°C<sup>7</sup>. Above 660°C, we noted decomposition of the InAs nanowires due to the volatility of As. For the lowest temperature growth, which was at 400°C, we noted a migration of the liquid alloy tip, as shown in Figure 2. This result strongly suggests that the tip is liquid even at a temperature below the bulk eutectic, allowing the growth to proceed by the



*Figure 2: Migration of liquid In-Au tip at 400 °C.*

well known VLS growth mechanism. We found, in general, that the length of the nanowires was controlled by the length of the annealing time at a set temperature, while the width of the nanowire was controlled by Au alloy size.

The HRTEM image of the nanowire, revealing the lattice fringes, is shown in Figure 3, with a scale bar of 5 nm. The insets show the corresponding selective area electron diffraction (SAED) pattern and the nanowire tip. The electron diffraction pattern shown was imaged down the [011] zone axis. From these results, the measured lattice spacing along the (111) direction is 0.344 nm,

corresponding to the lattice spacing of bulk InAs. HRTEM EDS performed on the nanowire is indicated equal atomic percent of In and As, confirming stoichiometric InAs.

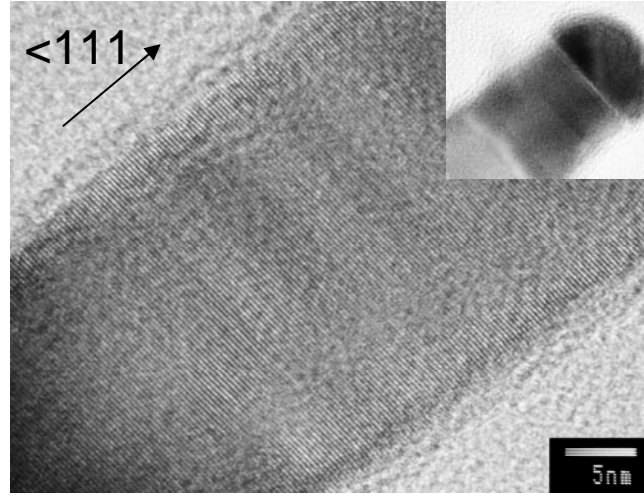


Figure 3: HRTEM image of an InAs nanowire, showing the lattice fringes and the In-Au metal tip.

### 3.2 Growth of InAs nanowire arrays on other substrates

We have also investigated the growth of InAs nanowires on other substrates, including InAs ( $5^\circ$  miscut from  $\langle 111 \rangle$ ), Si(111), as well as quartz and  $\text{SiO}_2$ . In all cases, we were able to grow

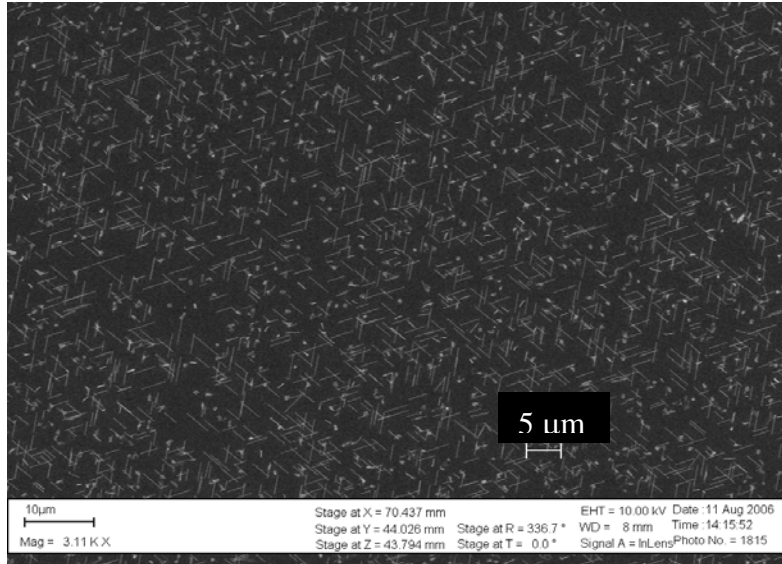


Figure 4: Growth of InAs nanowire array on InAs(111) miscut by  $5^\circ$  from the normal.

single crystal InAs  $\langle 111 \rangle$  nanowires, but they were inclined at different angles with respect to the substrate, depending on the substrate and the crystallography. In the case of growth on the  $5^\circ$  miscut InAs(111), the nanowires grew in an array of a triangular regular pattern inclined at an angle from the surface of the substrate, as shown in Figure 4. In this case, it appears that only part of the  $\langle 111 \rangle$  family of directions was able to grow, producing this triangular pattern. In the case of growth on Si(111), as shown in Figure 5a, one can see InAs nanowires which are randomly oriented, exhibiting no symmetry with the substrate. Again, these nanowires grew at an angle from the substrate and they thus do not lie on the substrate surface. The results are quite different when an amorphous substrate, such as  $\text{SiO}_2$  is used. As can be seen in Figure 5b, the nanowire growth originates from small InAs islands which nucleate on the substrate, allowing the nanowires to actually lie in the plane of the substrate.

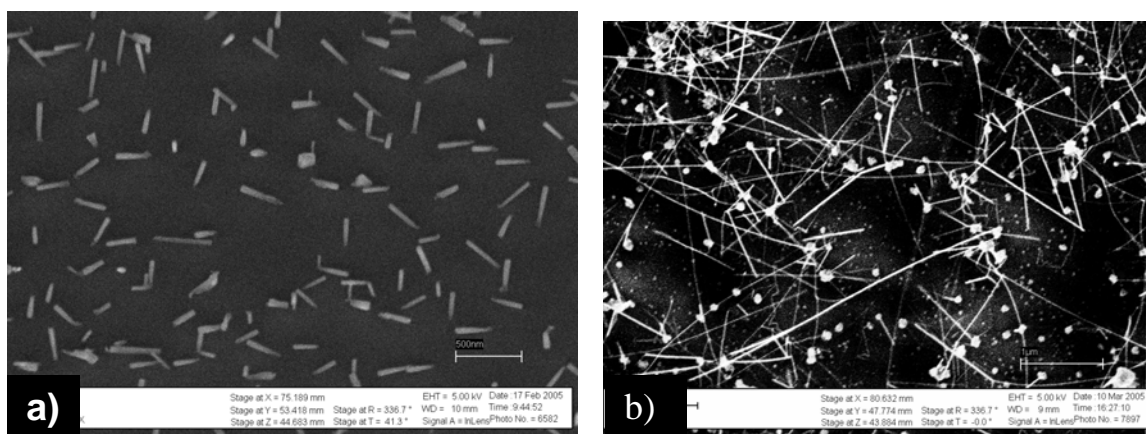


Figure 5: Growth of single crystal InAs nanowire arrays on a) Si(111) and b)  $\text{SiO}_2$ .

#### 4. PLASMONIC PROPERTIES of InAs/Ag NANOWIRE COMPOSITE ARRAYS

The detection of very small numbers of molecules in liquid or gaseous phases is of interest for both fundamental and applied reasons. A promising technique for sensing applications involves the use of Raman scattering (RS), which is an optical probe that can provide a unique fingerprint for the chemical or material being analyzed. In RS, the characteristic vibrational modes of a molecule are detected *via* the inelastic scattering of an incident laser line that occurs when these modes are

excited. This allows for unique identification of a molecule and provides information about the molecular bonding involved. However, a key issue for RS is that the cross-sections are very small. Typically, the intensity of a line due to inelastic scattering by a molecular vibration, relative to that of the elastically-scattered (Rayleigh) line, is  $\sim 10^{-8}$ . Hence, conventional RS is useable mainly for pure or highly concentrated samples.

It is well known that Raman scattering can be significantly enhanced for certain chemicals if they adsorb on nanostructured metal surfaces<sup>8-10</sup>. As the laser light reaches the nanostructured surface, it excites plasmons in these metal nanostructures, enhancing the local electric fields, which in turn couple with the dipoles of the adsorbed molecule. In addition, the local fields at the surface of the nanostructures are enhanced by the small dimensions involved. All of these effects lead to enhancements of the Raman scattering from the surface-adsorbed molecule by as much as  $10^{16}$  theoretically<sup>8-10</sup> and  $10^6$  experimentally<sup>8-10</sup>. However, the current situation is such that there is no comprehensive model to explain the SERS effect, and thus it is very difficult to design SERS-active substrates for a specific molecular species.

We have shown previously that  $\text{Ga}_2\text{O}_3/\text{Ag}$  nanowire composites can be very efficient SERS substrates<sup>11,12</sup>, and we have suggested that the nanowire crossings result in “hot” spots<sup>13</sup> in the electric fields, thus enhancing the SERS signal. Since we could not control the array geometry in the  $\text{Ga}_2\text{O}_3$  nanowire case, it was not possible to test this suggestion. However, as shown above, we are now able to grow a variety of nanowire geometries of InAs, owing to the availability of InAs(111) substrates, which allows us to grow straight, epitaxial, non-interacting nanowire arrays. When amorphous substrates are used, however, we can also produce flat, cross-over random geometries, similar to the  $\text{Ga}_2\text{O}_3$  nanowire case. Thus, tailoring the geometries lets us investigate the “hot” spot concept further.

In order to compare to the previous results, we have used  $10^{-6}$  M Rhodamine 6G (RH6G) for these studies. In case of our nanowire SERS substrate design, 40 nm InAs nanowires were produced using 40nm Au colloids, in two different types of arrays. The first array involved the formation of epitaxial, straight InAs nanowires on InAs (111), which did not exhibit crossings, as shown in Figure 6a. The second set of nanowires were grown on  $\text{SiO}_2$ , which resulted in a crossed, flat, random array, as shown in Figure 6b. In both cases, the InAs nanowires were covered with 5nm of



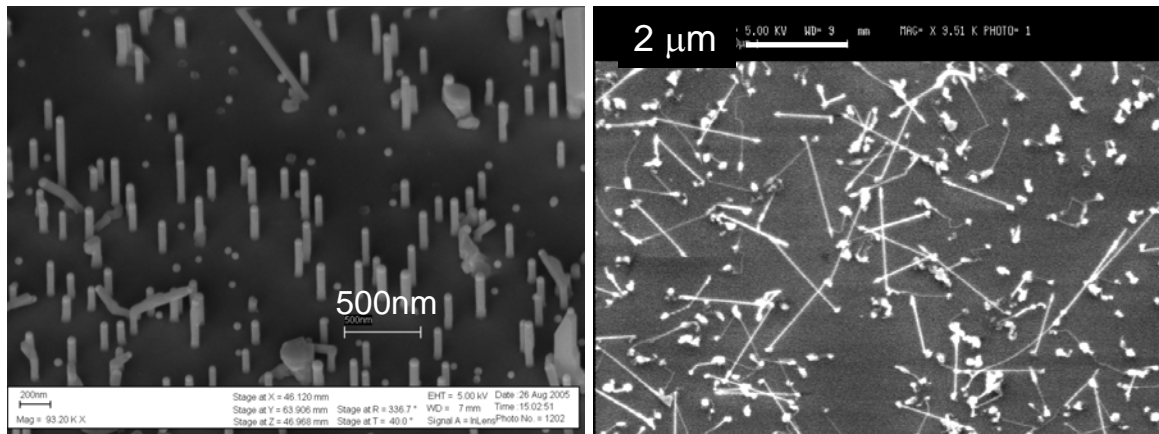


Figure 6: InAs nanowire array grown on a) InAs(111) and b) SiO<sub>2</sub>.

Ag (as in the previous experiments), forming InAs/Ag nanowire composite arrays. The Ag film on a flat substrate did not exhibit any SERS signal, which rules out the effect of Ag roughness as the source of the SERS signal.

A comparison of the SERS signal, using the Rh6G molecule and the 5145nm line of the Ar ion laser at less than 1 mW of power, is shown in Figure 7. The most obvious result is that the

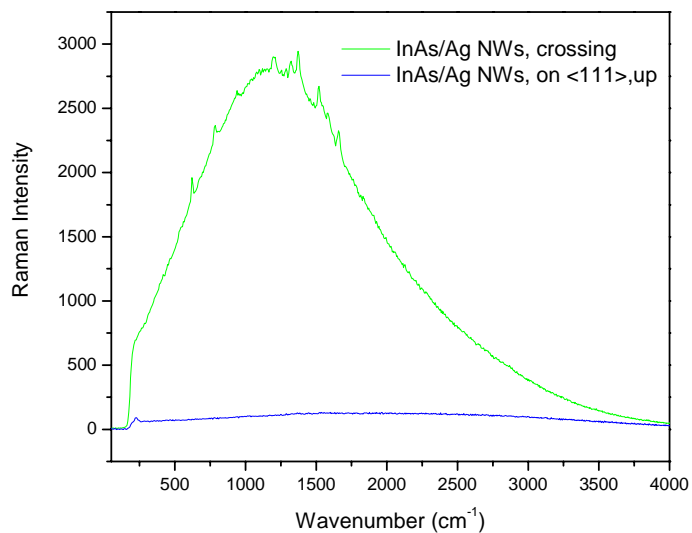


Figure 7: Comparison of the Raman spectra for crossed and parallel InAs/Ag nanowire composite arrays. Note the large surface enhanced fluorescence (SEFs) in addition to the SERS for the crossed wire geometry.

crossed array geometry shows not only a SERS signal typical for Rh6G, but a very strong surface enhanced fluorescence (SEFs) is also evident, characterized by the broad, intense luminescence centered near  $1500\text{ cm}^{-1}$ . The non-interacting wire array formed from parallel, InAs wires spaced farther apart, do not exhibit the characteristic SERS of Rh6G, nor is a SEFs signal evident. In both cases, a similar nanowire density was measured, ruling out a simple volume effect. These results suggest the importance of cross-over geometry in order to achieve a significant SERS enhancement, which is a result of the very high electric fields which can be achieved in this type of geometry.<sup>14</sup>

## 5. CONCLUSION

In conclusion, we have described a very simple method to grow InAs nanowire arrays by using a sealed quartz tube. Despite the simplicity, the new growth method yields single crystalline, stoichiometric InAs nanowires, which grow epitaxially on an InAs(111) substrate, and in variously oriented arrays, depending underlying substrate. In this way, we have been able to grow non-interacting InAs nanowire arrays, as well as flat, crossed arrays, which show significantly different SERS results using Rh6G as the sensing molecule. These results indicate that a crossed geometry leading to electric field “hot” spots can significantly enhance the SERS signal from target molecules.

## 6. REFERENCES

- <sup>1</sup> K. Hiruma, M. Yazawa, T. Katsuyama, K. Ogawa, K. Haraguchi, M. Koguchi, and H. Kakibayashi, J. Appl. Phys. **77**, (1995) 447.
- <sup>2</sup> L.E. Jensen, M.T. Bjork, S. Jeppesen, A.I. Persson, B.J. Ohlsson, and L. Samuelson, Nanolett. **4**, 10, (2004) 1961-1964.
- <sup>3</sup> X. Duan and C.M. Lieber, Adv. Mater. **12**, 4, (2000) 298.
- <sup>4</sup> M. He, M.M.E. Fahmi, S.N. Mohammad, R.N. Jacobs, L. Salamanca-Riba, F. Felt, M. Jah, A. Sharma, and D. Lakins, Appl. Phys. Letts. **82**, (2003) 21.
- <sup>5</sup> H. Park, S.M. Prokes and R.C. Cammarata, Appl. Phys. Lett. **87**, (2005) #063110.
- <sup>6</sup> Max Hansen, *Constitution of Binary Alloys*, (McGraw-Hill Book Company, New York, 1958) 211.
- <sup>7</sup> H.D. Park, A-C Gaillot, S.M. Prokes and R.C. Cammarata, J. Cryst. Growth, in press.

- <sup>8</sup> E. Hao and G.C. Schatz, J. Chem. Phys. **120**, (2004) 357.
- <sup>9</sup> M. Kerker, D.S. Wang, and H. Chew, Appl. Optics, **19**, (1980) 3373.
- <sup>10</sup> M. Moskovits, Rev. Mod. Phys. **57**, (1985) 783.
- <sup>11</sup> S.M. Prokes, W.E. Carlos and O.J. Glembocki, Proceedings of the SPIE, volume 6008 (2005) 60080C-1.
- <sup>12</sup> O.J. Glembocki, S.M. Prokes, H. Szemanski, J. Liu, F. Kub and C. Kub, Proceedings of the SPIE, volume 6008 (2005) 600809-1.
- <sup>13</sup> J. P. Kottmann and O. J.F. Martin, Optics Express, Vol. 8, No. 12, (2001) 655 - 663
- <sup>14</sup> S.M. Prokes, O.J. Glembocki, R. Rendell and M. Ancona, Appl. Phys. Lett., submitted.